Equilibrium Studies of Chromium(III) Complexes. I. The Complex Formation between Chromium(III) and Ethylenediamine in Aqueous Solution

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A new method is described whereby it is possible to establish equilibrium in aqueous solution between chromium(III) and different amine ligands (here ethylenediamine) within 3 − 5 days at room temperature as far as mononuclear complexes are concerned. The catalyst used is charcoal in combination with small amounts of chromium(II). A constant chromium(II) concentration is maintained by electrolytic reduction of chromium(III).

The hitherto unknown ion, Cr en$_2$en*(OH)$^{2+}$ (en≡ethylenediamine, en*≡en as a monodentate ligand) is one of the equilibrium species, and it was isolated in solution.

The stability constants for the formation of Cr en$_3$$^{3+}$ and Cr en$_2$(enH)(H$_2$O)$^{4+}$ from cis-Cr en$_2$(H$_2$O)$_2$$^{3+}$ were determined in 1 M chloride medium (NaCl) at 24 °C to be $10^{6.43}$ and $10^{0.0}$ M^{-1}, and the acid dissociation constants of Cr en$_2$(enH)(H$_2$O)$^{4+}$ to be $10^{-4.4}$ and $10^{-8.8}$ M. The gross stability constant for Cr en$_3$$^{3+}$ was found to be $10^{19.5}$ M^{-3} and the ratio between cis- and trans-Cr en$_2$(OH)$_2$$^{+}$ to be 5.

The equilibrated solutions contain several polynuclear species among which are the ions [en$_2$Cr(OH)$_2$Cr en$_2$]$^{4+}$ and the new [Cr{(OH)$_2$Cr en$_2$}$_3$]$^{6+}$ which we isolated as various salts. The latter is the chromium analogue of Werner's brown cobalt salt.

Attempts to study equilibria between chromium(III) and ligands in aqueous solution are complicated by the robustness of chromium(III) complexes. Therefore very little has been published in this field. Cobalt(III) complexes are in many ways analogous to those of chromium(III), and cobalt(III) likewise exhibits this robust behaviour. Bjerrum [1] showed, however, that it is possible to obtain equilibrium between

cobalt(III) and ammonia if charcoal is used as a catalyst, a method which has later been used with other ligands, among them ethylenediamine.[2]

It has been shown that charcoal reduces a little of the cobalt(III) to cobalt(II).[3-5] Charcoal alone does not seem to have any catalytic effect on chromium(III) but if chromium(II) is added as well, the robustness is strongly reduced.[6-8] This has been used in attempts to establish equilibrium between chromium(III) and ammonia by adding charcoal to concentrated ammonium chloride solutions containing different amounts of ammonia and all the chromium initially as chromium(II).[8] Chromium(II) alone, like charcoal alone, does not establish equilibrium in such solutions. When both are present, charcoal, besides its catalytic effect on chromium(III), also catalyzes the oxidation of chromium(II) by the medium:

$$Cr(II) + H(I) \overset{C}{\rightarrow} Cr(III) + H(0) \qquad (I)$$
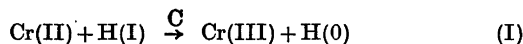
This has the disadvantage that all chromium(II) may disappear before equilibrium is reached.

We present here a new method based on the same catalyst, i.e. chromium(II) and charcoal. By electrolytic reduction of chromium(III) to chromium(II) it is possible to maintain a constant concentration of chromium(II) because a steady state is reached when the amount of chromium(II) removed by reaction I equals the amount generated by electrolysis. In this way it is possible to choose a suitable catalyst

concentration and keep it for days without any changes in the medium, except for a small H(I) consumption due to the continuous reduction.

We have applied the method to several chromium(III) complex equilibria. This paper concerns the equilibria between chromium(III) and ethylenediamine. Such equilibria have been studied before mainly by Woldbye,[9] who determined the ratio between cis- and trans-[Cr en$_2$-(OH)$_2$]$^+$ (en≡ethylenediamine) and measured the acid dissociation constants for the diaqua and hydroxo aqua tetramine complexes.

EXPERIMENTAL

Procedure. A typical experiment was carried out as follows. A 100 ml flask was equipped with an inlet and outlet for nitrogen gas freed from oxygen by a washing-flask with Cr(II)-solution. At the bottom of the 100 ml flask were two mercury electrodes which could be filled with pure mercury from outside. One mercury electrode served as cathode in combination with a platinum anode separated from the cathode chamber (containing the chromium(III) solution) by the membrane of a Radiometer K 401 calomel electrode. The other mercury electrode, together with a saturated calomel electrode, registered the emf of the solution. Furthermore, the flask was provided with a thermometer, a valve for taking out samples without letting in oxygen, and a magnetic stirrer. The gas outlet ended under water or ethanol so that with a calibrated gas burette it was possible to measure the volume of hydrogen evolved.

The 50 – 100 ml solutions containing chromium(III) and ligands were placed in the cathode chamber. The compositions of such solutions are given in Fig. 1 and Table 1. In the anode chamber we used 2 M H$_2$SO$_4$, so that the current through the membrane was mainly established by hydrogen ions, in order to make the pH-change in the chromium solution as small as possible. After addition of charcoal and after removal of oxygen a voltage of about 10 V was applied, giving rise to a current of 5 – 15 mA. After 0.5 – 1 h the emf dropped to *ca.* – 1.1 V and a distinct change in the solution had then taken place. The hydrogen evolved, now equivalent to the current, maintained a slight overpressure in the flask, which was kept like this, *i.e.* with [Cr(II)]/[Cr(III)]≃0.01, for 3 – 5 days. At this time equilibrium was reached and the current was switched off. The solution was analyzed when the small amount of chromium-(II) had been oxidized to chromium(III) by the medium. The robustness of chromium(III) facilitated the further investigations of such solutions.

All the experiments were carried out at (24 ± 1) °C. The amount of charcoal and the current could be varied within wide limits, but the use of 1 – 2 g of charcoal *per* l and the above-mentioned conditions were found to produce the best catalytic effect.

Analysis of the medium and of the distribution of chromium(III) complexes in the equilibrium solutions. The solutions were analyzed for the total content of chloride, nitrogen (Kjeldahl) and chromium (atomic absorption spectrophotometry) before and after equilibration; the pH of the solutions was measured with a glass electrode and the amount of basic components was determined by titration with 0.1 M hydrochloric acid. The amounts of different chromium(III) species were determined by atomic absorption spectrophotometry after separation by cation-exchange chromatography on columns of Sephadex SP-C-25. No significant changes in the medium were observed. Initial difficulties with some solutions losing chromium during the reaction were overcome by thorough rinsing of the equipment. The most important results of these analyses are given in Fig. 1 and in Tables 1 and 2.

Table 1. The composition of the solutions having [Cl$^-$] = 1.0 M (NaCl). The determination of the concentrations of free enH$_2$$^{2+}$, enH$^+$, and en are based on a total nitrogen analysis (Kjeldahl), a correction for coordinated en, on our determination of the acid dissociation constants of enH$_2$$^{2+}$ (Table 3), pH$_{exp}$, and on a determination of basic components by titration with 0.1 M HCl. "tris" and "bis" refer to [Cr en$_3$]Cl$_3$.3H$_2$O and trans-[Cr en$_2$Cl$_2$]Cl.H$_2$O, respectively.

Experiment No.	1	2	3	4	5	6	7	8	9	10
Final pH$_{exp}$	8.54	9.01	9.16	9.71	9.71	9.76	9.78	9.78	10.48	10.49
Total conc. of N (M)	1.05	1.17	1.10	1.03	1.13	1.02	1.04	1.02	2.88	2.92
[enH$_2$$^{2+}$] (mM)	44	16	11							
[enH$^+$] (mM)	456	517	476	367	404	353	355	348	461	460
[en] (mM)	10.9	36.6	47.6	130	143	141	148	145	964	983
C_{Cr} (mM)	10.65	15.76	10.25	13.7	9.82	13.30	11.45	13.7	6.2	15.9
Initial Cr(III)-comp.	tris	bis	tris	tris	bis	tris	bis	bis	tris	tris

Table 2. The content, in mol-%, of the mononuclear complexes relative to the total chromium(III) content. CrN_4O_2 refers to the sum of *cis-* and *trans-*Cr en$_2$ (OH)$_2^+$ and *cis-* and *trans-*Cr en$_2$(OH)(H$_2$O)$^{2+}$; CrN_5O is the sum of Cr en$_2$en*(OH)$^{2+}$ and Cr en$_2$(enH)(OH)$^{3+}$. The hydrolysis constants for reactions II and III are given at the bottom of the table. ( ) denote analyses repeated after one year.

Exp. No.	1	2	3	4	5	6	7	8	9	10
% CrN_4O_2	58	79	87(84)	93	92	93	93	95	100	98
% *cis*-Cr en$_2$(OH)$_2^+$	46.0	64.7	71.7	77.5	76.7	77.5	77.5	79.2	83.3	81.7
% CrN_5O	4.0	2.8	3.0(3.1)	1.83	2.8	2.1	3.1	1.76	1.06	1.5
% Cr en$_2$en*(OH)$^{2+}$	1.42	1.73	2.06	1.63	2.49	1.89	2.81	1.59	1.04	1.47
% Cr en$_3^{3+}$	8.8	5.9	3.1(3.0)	0.99	1.0	1.0	1.0	1.0		
$K_{h6/cis4}$ (M) [a]	100	80	112	81	88	69	66	66		
$K_{h5/cis4}$ (M) [b]	14.8	19.3	16.5	17.4	12.5	14.5	9.8	17.3	36.9	25.6
$K_{h6/trans4}$ (M)	Average: 16.6									
$K_{h5/trans4}$ (M)	Average: 3.7									

[a] Average 83. [b] Average 18.5.

The separations on cation-exchange columns of Sephadex SP-C-25 are described in the following in more detail. The separations were made in acid as well as in basic solution on columns 1.2 cm in diameter and *ca.* 5 cm long, protected from light when necessary. During the separation solutions were cooled in ice to prevent further reaction and separations were carried out as fast as possible ($\frac{1}{2}$ – 1 h).

For the acid separation 5 ml of the equilibrium solution ($C_{Cr} = 0.01 - 0.02$ M) were diluted with water (0 °C) to 100 ml and acidified with hydrochloric acid to pH $\simeq$ 3. This solution was applied to the column with 0.5 – 1 atm overpressure and eluted with sodium chloride solutions of concentrations increasing from 0.2 to 2.0 M (pH $\simeq$ 3). This divided the chromium mixture into several bands of cations with increasing charge, at least as regards mononuclear complexes. The first contained *cis-* and *trans-*Cr en$_2$(H$_2$O)$_2^{3+}$ and Cr en$_3^{3+}$, the second Cr en$_2$(enH)(H$_2$O)$^{4+}$ (see later) and en$_2$ Cr(OH)$_2$-Cr en$_2^{4+}$. In the following 4 – 5 violet bands it was not possible to identify any mononuclear complexes. These bands are therefore assumed to contain polynuclear complexes exclusively.

For the basic separation 5 ml of the equilibrium solution were diluted with water (0 °C) to 75 ml. After application to the column it was eluted with an ammonium chloride-ammonia buffer with [NH$_3$] = 0.1 M and [NH$_4^+$] increasing from 0.15 to 2.0 M. This divided the mixture into the following bands of mononuclear complexes with increasing charge: A first band containing *cis-* and *trans-*Cr en$_2$(OH)$_2^+$, a second containing Cr en$_2$en*(OH)$^{2+}$ (see later), and a third one containing Cr en$_3^{3+}$. At the bottom of this band was a band of en$_2$Cr(OH)$_2$Cr en$_2^{4+}$ mixed with another unidentified polynuclear complex. The subsequent violet bands (up to four) contained polynuclear species. In this basic separation a few per cent of the chromium

remained on the column, even after elution with 2 M NH$_4$Cl.

From these two methods of separation and a combination of them it was possible, by chromium atomic absorption spectrophotometry, to determine the amounts of most of the different chromium species in the equilibrated solutions.

Identifications of the chromium(III) complexes. Several methods were used to identify the chromium species and to verify that the separate bands did not contain significant amounts of undetected species. Visible spectrophotometry and analyses of the molar ratio between chromium and nitrogen after removal of nitrogen not bound to chromium were performed directly on the eluates. It was possible to obtain eluates rather concentrated with respect to chromium by applying a less concentrated eluate to a new short column after this less concentrated eluate had been diluted further 5 – 10 times. By eluting this short column with a concentrated (2 – 4 M) electrolyte we obtained eluates with [Cr(III)] $\simeq$ 0.1 – 0.2 M. These eluates were very suitable for precipitations of salts and in this way we isolated, among others, salts of Cr en$_3^{3+}$ and some of the polynuclear complexes (see later) which could then be further analyzed.

The eluates with high chromium concentrations were also suitable for ESR spectroscopy. Such eluates were diluted × 2 with glycerol and cooled to – 130 °C within 1 – 2 min, after which the ESR spectrum of the frozen glass was taken. Such spectra appeared to be good fingerprints which could be compared with those of known chromium(III) complexes, and they also served as a convenient means to determine the ratio between *trans-* and *cis-*Cr en$_2$(H$_2$O)$_2^{3+}$ (see Fig. 3).

Other properties, in addition to the methods mentioned above, contributed to the identification of the complexes, among them the acid-

Table 3. Relevant acid dissociation constants determined by glass electrode measurements. pK_{S2pen} for Cr en$_2$(enH)(H$_2$O)$^{4+}$ was determined on the basis of elution rates (see Fig. 5).

Acid (abbr.)	pK_{S1}	pK_{S2}	Medium	Reference
enH$_2$$^{2+}$	7.52	10.16	1 M Cl$^-$ (NaCl)	This work
	7.49	10.17	1 M KNO$_3$	Poulsen & Bjerrum [23]
	7.44	10.06	1 M KCl	Pecsok & Bjerrum [14]
Cr en$_2$(enH)(H$_2$O)$^{4+}$	4.4		1 M NaCl	This work
(pen)		8.8	0.25 M NH$_4$Cl	This work
cis-Cr en$_2$(H$_2$O)$_2$$^{3+}$	4.80	7.17	1 M NaNO$_3$	Woldbye [9]
(*cis*)				
trans-Cr en$_2$(H$_2$O)$_2$$^{3+}$	4.08	7.49	1 M NaNO$_3$	Woldbye [9]
(*trans*)				

base properties (see Table 3) and the elution rates which, as mentioned above, gave an indication of the charge.

Determination of the chromium(II) content during the equilibration. This and other investigations [8,10] show that it is possible to use mercury as an inert electrode in order to measure the potential in solutions such as the equilibrium mixtures described here. With a mercury electrode it was possible to follow the potential during equilibration, and when equilibrium was obtained it was possible to measure the potential and at the same time determine the chromium(II) concentration (see Fig. 4) by one of the following methods.

The content of chromium(II), [Cr(II)]$_0$, in the steady state, where the amount of chromium(II) generated by electrolysis equals that removed by the charcoal-catalyzed oxidation to chromium(III), was determined by measuring the volume of hydrogen evolved, according to eqn. I, after stopping the electrolysis.

[Cr(II)]$_0$ was also determined by measuring the current, I, in the steady state and $(\partial E/\partial t)_0$ after stopping the electrolysis (see Fig. 4). From $E = E' + (RT/F) \ln [\text{Cr(III)}]/[\text{Cr(II)}]$, assumed to be valid under our conditions for the total concentration of Cr(III) and Cr(II), one finds by differentiation with respect to time, t, and substituting [Cr(III)] = C_{Cr} − [Cr(II)]:

$$\frac{\partial E}{\partial t} = - \frac{RT}{F} \frac{C_{Cr}}{[\text{Cr(II)}]\{C_{Cr} - [\text{Cr(II)}]\}} \frac{\partial [\text{Cr(II)}]}{\partial t}$$

The rate of oxidative removal of chromium(II) at $t=0$ is thus $(\partial[\text{Cr(II)}]/\partial t)_0 = -(F/RT)[\text{Cr(II)}]_0(\partial E/\partial t)_{t \to 0+}$ (when $C_{Cr} \gg [\text{Cr(II)}]$), which in the steady state equals the rate at which chromium(II) is generated by electrolysis, *i.e.* $I/(F V_{sol})$ where V_{sol} is the volume of the solution.

Thus $[\text{Cr(II)}]_0 = \dfrac{RTI}{F^2 V_{sol}(\partial E/\partial t)_0} =$

$0.0158 \dfrac{I}{V_{sol} \cdot (\partial E/\partial t)_0}$ at 24 °C,

where I is in mA, V_{sol} in ml and $(\partial E/\partial t)_0$ in mV/min.

We have several reasons to believe that all the current is used for the reduction of chromium(III) to chromium(II) namely the good agreement between the two methods, and the
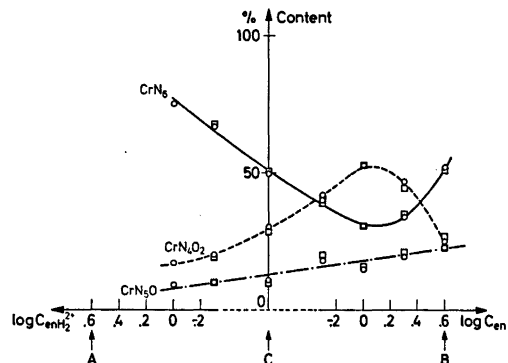

Fig. 1. The content, in mol per cent, of Cr en$_3$$^{3+}$ (———— CrN$_6$), Cr en$_2$en*(OH)$^{2+}$ + Cr en$_2$enH(OH)$^{3+}$ (− · − CrN$_5$O), and Cr en$_2$(OH)$_2$$^+$ (− − CrN$_4$O$_2$) as a function of log C_{en} and log $C_{en.2HCl}$. C_{Cr} = 0.05 M and $C_{en.HCl}$ = 4 M. The distance AB is set to 2.6 log units, *i.e.* the difference between the acid dissociation constants pK_{S2enH2} and pK_{S1enH2} found by pH-measurements in the neighbourhood of the point C referring to a solution of 4 M ethylenediamine hydrochloride. [Cr en$_3$]Cl$_3$.3H$_2$O ($\square$) and *trans*-[Cr en$_2$Cl$_2$]Cl.H$_2$O (O) were used as starting materials.
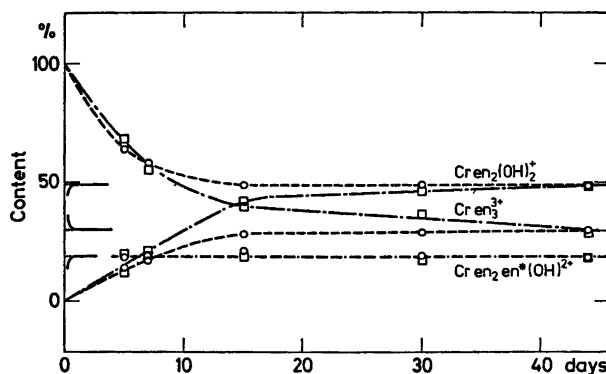
Fig. 2. The content, in mol per cent, of Cr en$_3$$^{3+}$, Cr en$_2$en*(OH)$^{2+}$ and Cr en$_2$(OH)$_2$$^+$ as a function of time. $C_{Cr} = 0.05$ M, $C_{en.HCl} = 4$ M, and $C_{en} = 2$ M.
— · — □: Uncatalyzed starting with [Cr en$_3$]Cl$_3$· 3H$_2$O;
— — — ○: uncatalyzed starting with *trans*-[Cr en$_2$Cl$_2$]Cl.H$_2$O;
————: catalyzed starting with [Cr en$_3$]Cl$_3$.3H$_2$O;
· · ·: catalyzed starting with *trans*-[Cr en$_2$Cl$_2$]Cl· H$_2$O.

fact that the hydrogen evolution, when starting with [Cr(II)] = 0, increases slowly until the steady state is reached, whereas no hydrogen is evolved when there is no charcoal present. Finally, addition of known amounts of chromium(II) sulfate confirmed the validity of both methods.

Chemicals and apparatus. All chemicals used were reagent grade or analyzed by us. [Cr en$_3$]-Cl$_3$.3H$_2$O,[11] *trans*-[Cr en$_2$Cl$_2$]Cl.H$_2$O,[12] *cis*-[Cr en$_2$-(H$_2$O)$_2$]Br$_3$,[13] and *trans*-[Cr en$_2$(OH)(H$_2$O)]Br$_2$.H$_2$O [12] were prepared according to or analogously to the reference methods and were analyzed for Cr, N, and halogen. All analyses agreed within $1 - 2$ % (relative) with the given formulae. The charcoal used was a Norit W product.
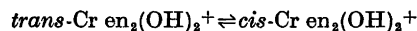
Visible spectra were taken on a Cary 14 or a Bausch and Lomb Spectronic 505 recording spectrophotometer, and ESR spectra on a Jeol JES-ME-1X. A Perkin-Elmer 403 Atomic Absorption Spectrophotometer was used for chromium analysis. All emf and pH measurements were performed with a Radiometer PHM 52, the G 202 C glass electrodes used being tested in the relevant media according to Bjerrum.[1]

RESULTS

Equilibria studied. We have studied the following hydrolysis equilibria:

Cr en$_3$$^{3+}$ + en + 2 H$_2$O $\rightleftharpoons$
Cr en$_2$(OH)$_2$$^+$ + 2 enH$^+$ (II)
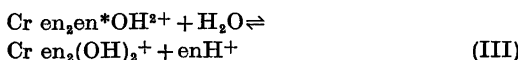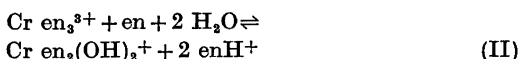
Cr en$_2$en*OH^{2+} + H$_2$O $\rightleftharpoons$
Cr en$_2$(OH)$_2$$^+$ + enH$^+$ (III)

and in addition to these the *cis-trans* equilibrium:

trans-Cr en$_2$(OH)$_2$$^+$ $\rightleftharpoons$ *cis*-Cr en$_2$(OH)$_2$$^+$

These are equilibria between well known species with the exception of Cr en$_2$en*OH^{2+}, where en* denotes en binding as a monodentate ligand. A more detailed description of the properties of this complex, which is able to take up two protons, is given later in this section.

Fig. 1 gives the results of equilibration in 4 M ethylenediamine hydrochloride. In this medium the predominant complexes are the three mononuclear ones shown. No hydrolysis constants are given as the medium is far from constant, especially at high [enH$_2$$^+$] and high [en]. The ratio between *cis*- and *trans*-Cr en$_2$(OH)$_2$$^+$ was found to be *ca.* 10 by ESR measurements (see later).

Equilibrium was also achieved without catalysis in solutions with the same initial composition as those in Fig. 1 with log $C_{en} = 0.3$. Fig. 2 shows these catalyzed and uncatalyzed equilibrations and gives an impression of the increase of rate due to the catalyst. It is seen that the same final composition is reached independent of the choice of initial chromium compound and of whether the catalyst is used or not.
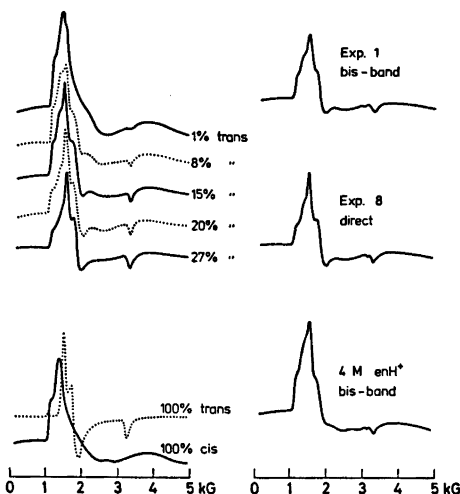
Fig. 3. First derivative ESR spectra of frozen glasses ($-130\,°C$) at 9.3 GHz. The medium was a 1:1 mixture of glycerol and 2 M LiCl (exp. 8: 1 M NaCl) with $[H^+] \simeq 0.001 - 0.01$ M and $C_{Cr} = 0.01 - 0.1$ M.

Left: Mixtures of *cis*- and *trans*-Cr en$_2$(H$_2$O)$_2$$^{3+}$ from *cis*-[Cr en$_2$(H$_2$O)$_2$]Br$_3$ and *trans*-[Cr en$_2$(OH)(H$_2$O)]Br$_2$.H$_2$O, respectively (% = mol per cent).

Right: Spectra of the acid ion-exchange bands from exp. 1 (Tables 1 and 2) and from a 4 M enH$^+$-exp. (Fig. 1), containing *cis*-and *trans*-Cr en$_2$(H$_2$O)$_2$$^{3+}$, eluted with 2 M LiCl. In the middle is shown the spectrum of the unseparated equilibrium solution from exp. 8 after addition of hydrochloric acid.

In order to determine the stability constants for chromium(III) and ethylenediamine we made a series of experiments in a constant ionic medium where the chloride concentration was kept at 1 M with sodium chloride. The compositions of the solutions in this series are given in Table 1. During the equilibration the pH varied at most 0.1 pH-unit. When analysis showed that there had been no change in the amounts of the different chromium complexes for a day or two the catalysis was stopped. The results of a final analysis of the content of Cr en$_3$$^{3+}$, CrN$_5$O, and CrN$_4O_2$ are given in Table 2.

The ratio between *cis*- and *trans*-CrN$_4$O$_2$ was determined from ESR spectra of frozen glasses of the CrN$_4$O$_2$-eluate and also of solutions Nos. 7 − 10 without preceding separation (Fig. 3). We did not succeed in separating *cis*- and *trans*-CrN$_4$O$_2$ by ion-exchange chromatography but

the ESR spectra enabled us to detect even small amounts of *trans* in *cis*, as shown in Fig. 3. The content of *trans* in CrN$_4$O$_2$ was measured to be between 15 and 19 % in the series, corresponding to

$$q_2 = [\text{cis-Cr en}_2(\text{OH})_2{}^+]/[\text{trans-Cr en}_2(\text{OH})_2{}^+] = 5$$

in good agreement with Woldbye's result.[9]

We determined the acid dissociation constants of enH$_2$$^{2+}$ and of Cr en$_2$(enH)(H$_2$O)$^{4+}$ in media similar to those used in exp. 1 − 10. The results are given in Table 3 together with relevant constants determined by other workers.

With $q_2 = 5$ and with the aid of Table 3 it is possible to calculate the equilibrium amounts of Cr en$_2$(enH)(OH)$^{3+}$ and of Cr en$_2$en*(OH)$^{2+}$ comprising the CrN$_5$O-eluates, as well as the amounts of *cis*- and *trans*-Cr en$_2$(OH)H$_2$O^{2+} and *cis*- and *trans*-Cr en$_2$(OH)$_2$$^+$ comprising the CrN$_4$O$_2$-eluates. This is done in Table 2.

From the analytical results in Tables 1 and 2 it is now possible to calculate the hydrolysis constants for reactions II and III, that is

$$K_{h6/cis4} = \frac{[\text{cis-Cr en}_2(\text{OH})_2{}^+][\text{enH}^+]}{[\text{Cr en}_3{}^{3+}][\text{en}]}$$

and the analogous $K_{h6/trans4}$ and

$$K_{h5/cis4} = \frac{[\text{cis-Cr en}_2(\text{OH})_2{}^+][\text{enH}^+]}{[\text{Cr en}_2\text{en*(OH)}^{2+}]}$$

and the analogous $K_{h5/trans4}$.

These constants for the exp. 1 − 10 are given in Table 2.

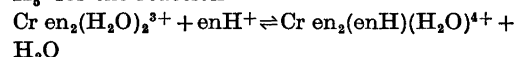The 3rd consecutive stability constant, K_3, for the reaction Cr en$_2$(H$_2$O)$_2$$^{3+}$ + en ⇌ Cr en$_3$$^{3+}$ + 2H$_2$O is derived from Tables 2 and 3:

$$K_{3cis} = \frac{[\text{Cr en}_3{}^{3+}]}{[\text{cis-Cr en}_2(\text{H}_2\text{O})_2{}^{3+}][\text{en}]} = $$

$$\frac{K_{S1cis}\,K_{S2cis}}{K_{S2enH2}\,K_{h6/cis4}}$$

giving $K_{3cis} = 10^{6.43}$ M^{-1} and analogously $K_{3trans} = 10^{7.53}$ M^{-1}.

K_5' for the reaction Cr en$_2$(H$_2$O)$_2$$^{3+}$ + enH$^+$ ⇌ Cr en$_2$(enH)(H$_2$O)$^{4+}$ + H$_2$O is also derived from Tables 2 and 3:

$$K'_{5cis} = \frac{[\text{Cr en}_2(\text{enH})(\text{H}_2\text{O})^{4+}]}{[\text{cis-Cr en}_2(\text{H}_2\text{O})_2{}^{3+}][\text{enH}^+]} = $$

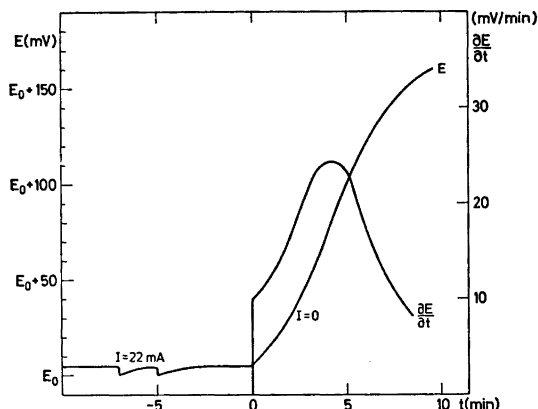$$\frac{K_{S1cis}\,K_{S2cis}}{K_{h5/cis4}\,K_{S1pen}\,K_{S2pen}}$$

Fig. 4. The electrode potential, measured between a mercury electrode and a saturated calomel electrode, for a typical experiment as a function of time, and its first derivative.

giving $K'_{5cis} = 10^{0.0}$ M^{-1} and analogously $K'_{5trans} = 10^{1.1}$ M^{-1}.

The gross stability constant from emf-measurements. During the equilibration period the electrode potential, E, between a mercury electrode and a saturated calomel electrode was followed continuously. Typical behaviour is shown in Fig. 4. The solution was at the final state of equilibration, and at -7 and -5 min a pure mercury surface was established by addition of new mercury to the electrode. E in the steady state, E_0, was measured as the lower points at -7 and -5 min, and [Cr(II)] at $t=0$ was calculated from $(\partial E/\partial t)_0 = 10$ mV/min (see exp. section) to be 0.35 mM. Measurement of the volume of hydrogen evolved between $t=0$ and $t=10$ min (0.42 ml) gave [Cr(II)] = 0.34 mM. Table 4 shows the measurements on solutions $1-3$ in their final state of equilibration. From these data one can estimate the stability constant β_{2cis} for the reaction Cr(H$_2$O)$_6^{3+}$ + 2en$\rightleftharpoons$*cis*-Cr en$_2$(H$_2$O)$_2^{3+}$ + 4H$_2$O:

$$\log \beta_{2cis} = \log \beta_2^{II} + pK_{S1cis} + pK_{S2cis} - 2pK_{S2enH_2} - (E_0 + 652)/59 +$$
$$\log \frac{[cis\text{-Cr en}_2(OH)_2^+][enH^+]^2}{[en]^2[Cr(II)]}$$

where β_2^{II} is the gross stability constant for the uptake of 2 en by Cr^{2+}. log β_2^{II} has been determined to be 9.19 in 1 M KCl,[14] and nearly all the Cr(II) will be present as Cr en$_2^{2+}$ in exp. $1-10$. "652" is the sum of the standard potentials of the Cr^{2+} − Cr^{3+} couple and of the

saturated calomel electrode (410 mV [15] and 242 mV, respectively). The pK$_S$ values are given in Table 3. Table 4 gives the values of log β_{2cis} as found from the emf-measurements.

The gross stability constant for Cr^{3+} binding 3 en is then given by $\beta_3 = \beta_{2cis} K_{3cis} = 10^{19.5}$ M^{-3}.

Table 4. log β_{2cis} determined from measurements of [Cr(II)] and the electrode potential E_0 between a mercury and a saturated calomel electrode in solutions $1-3$ at their final state of equilibration.

Exp. No.	$-E_0$ (mV)	[Cr(II)] (mM)	log β_{2cis}	
1	1133	0.39	13.32	
	1139	0.91	13.06	
	1187	1.92	13.55	13.38
	1139	0.35	13.47	
	1140	0.34	13.50	
2	1128	0.35	12.67	
	1145	0.47	12.83	
	1160	0.80	12.85	
	1134	0.50	12.61	12.74
	1160	0.55	13.01	
	1135	0.68	12.50	
	1150	0.69	12.74	
3	1166	0.31	12.92	
	1175	0.37	12.99	
	1142	0.150	12.83	12.99
	1120	0.025	13.23	
		Average of exp. Nos. $1-3$:		13.04
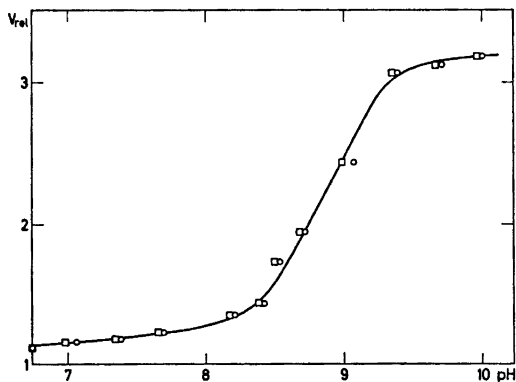
Fig. 5. The elution rate on Sephadex SP-C-25, V_{rel}, of Cr en$_2$(enH)(OH)$^{3+}$ + Cr en$_2$en*(OH)$^{2+}$ relative to that of Cr en$_3^{3+}$ as a function of pH. The eluting agent was 0.25 M NH$_4$Cl with varying concentrations of NH$_3$. pH was measured with a glass electrode (tested in this same medium according to Bjerrum [1]) before (O) and after (□) elution.

The Cr en$_2$(enH)(H$_2$O)$^{4+}$ ion and its deprotonated forms. This ion, believed to be an intermediate in the acid hydrolysis of Cr en$_3^{3+}$ [16] and recently found as such in this laboratory,[17] is, in its two basic forms, among the mononuclear complexes present in the equilibrium solutions dealt with above. As it has not been described in the literature so far, we shall give here a few details. The acid dissociation constants of the protonated ion are given in Table 3. Owing to the lower robustness in basic solution pK_{S2} was determined from the elution rate relative to that of Cr en$_3^{3+}$, using 0.25 M NH$_4$Cl with varying concentrations of ammonia as eluent (Fig. 5), because we found that robustness of many of the complex ions is significantly higher when bound to the resin. A similar magnitude of pK_S for enH$^+$ bound to chromium(III) has been found for (NH$_3$)$_5$Cr(OH)-(NH$_3$)$_4$enH^{6+}, namely 8.42 in 0.1 M KCl at 20 °C.[18]

The visible spectra of the ions are shown in Fig. 6. The visible spectrum and the ESR spectrum of Cr en$_2$(enH)(H$_2$O)$^{4+}$ are identical with those of the acid hydrolysis product of Cr en$_3^{3+}$.[17] Attempts to isolate salts of the ions resulted only in an amorphous, hygroscopic powder, most of which changed within hours into Cr en$_3^{3+}$ salt. Thus, out of the two possible

isomers we believe that we are dealing mainly with the one having enH$^+$ (en*) and H$_2$O (OH) *cis* to each other.

Polynuclear complexes. It appears that the mononuclear complexes quoted in Table 2 only form part of the total chromium(III) content. The ion-exchange separations showed at least five other bands, presumably all consisting of polynuclear complexes. It has not yet been possible to determine any equilibrium constants involving polynuclear complexes owing to the difficulties in separating and identifying them. Similar investigations with ammonia as ligand show [10] that equilibrium is established much more slowly, if at all, among the polynuclear than for the mononuclear complexes.

While the visible spectra of the polynuclear species isolated in solution by ion-exchange chromatography only show small differences, the ESR spectra of their frozen glasses have served as a very useful means of identification and recognition as they are often very different. The content of polynuclear species increases with increasing [Cr(III)] and increasing [H$^+$] and two of them have been identified, *viz.* the diol, en$_2$Cr(OH)$_2$Cr en$_2^{4+}$, which was isolated as the iodide, and Cr{(OH)$_2$Cr en$_2$}$_3^{6+}$, the chromium analogue of the tetranuclear cobalt(III) complex

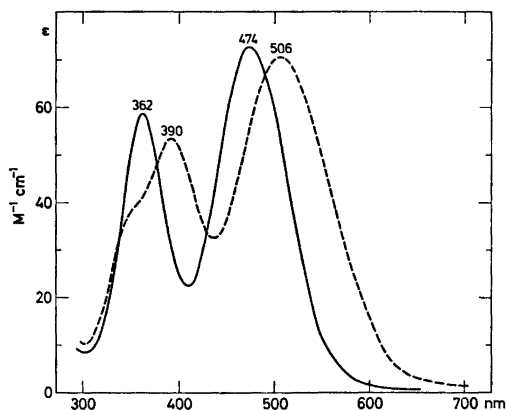*Fig. 6.* The visible spectra of Cr en$_2$(enH)-(H$_2$O)$^{4+}$ (———) and Cr en$_2$en*(OH)$^{2+}$ (- - -) in 2 M LiCl. The former spectrum was measured directly on a 2 M LiCl eluate of Cr en$_2$(enH)-(H$_2$O)$^{4+}$ from Sephadex SP-C-25, and the latter after addition of 12 M NH$_3$ to give [NH$_3$] = 0.5 M. Both spectra were measured twice with an interval of 5 min, and no changes were observed.

Table 5. Comparison of stability constants for Cr(III), Co(III), and Ni(II) with en.

	log K_1	log K_2	log K_3	log β_3	Ref.
Cr(III)			6.4 ≤ 6.2	19.5	This work Woldbye [9]
Co(III)			13.3	48.7	Bjerrum & Rasmussen [2] Woldbye [9]
Ni(II)	7.51	6.35	4.42	18.3	Poulsen & Bjerrum [23]

often referred to as Werner's brown salt.[19] We discovered this tetranuclear ion through its hydrolysis products in concentrated perchloric acid, and isolated the nitrate and iodide.[20] A more detailed report of our investigations of polynuclear chromium(III) complexes will be published later.[10]

DISCUSSION

From the results obtained we conclude that equilibrium among the mononuclear chromium(III) ethylenediamine complexes is indeed achieved by this catalytic procedure. We emphasize, in support of this conclusion, that the necessary condition is fulfilled that no further change is observed after some time. The final distribution of mononuclear complexes is independent of the initial chromium(III) compounds used and no difference in distribution is observed if the catalyst is not used at all (Fig. 2). Table 2 shows in addition a repeated analysis of the solution from exp. 3 after a year without catalyst. The differences from the first analysis are within the experimental error. Finally, the law of mass action is well obeyed, permitting the determination of the stability constants described in the previous section. The mercury electrode used for emf-measurements seems to work satisfactorily. This has been confirmed by similar investigations with, among others, ammonia and EDTA as ligands.[7,10] The high overvoltage of mercury towards hydrogen prevents the evolution of hydrogen in all these cases.

Fig. 2 illustrates the catalytic effect of Cr(II) and charcoal in 4 M ethylenediamine hydrochloride. Woldbye's investigation of the ethylenediamine system [9] shows that in a solution very similar to exp. 6−8 (NO_3^- instead of Cl^-)
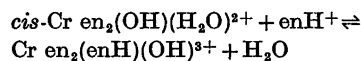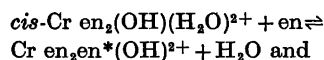
equilibrium is not reached within 50 days starting with Cr en$_3^{3+}$, whereas the present method requires only 3−5 days. The *cis-trans* equilibrium is established without catalysis within a few days according to Woldbye.[9]

Table 5 compares the equilibrium constants resulting from this investigation with other relevant constants. Chromium(III) is intermediate in stability between nickel(II) and cobalt(III), lying nearer to nickel(II). This same behaviour is observed with ammonia or EDTA as ligand.[10]

Our value of $K_3 \left(\dfrac{1}{K_3} = \dfrac{1}{K_{3cis}} + \dfrac{1}{K_{3trans}} \right)$

agrees reasonably well with Woldbye's estimate [9] of $K_3 \leq 10^{6.2}$ (owing to a calculation error the reference quotes $K_3 \leq 10^{10.2}$), which is based on the assumption that there is less than 0.5 % Cr en$_3^{3+}$ in his solutions. We find, using $K_3 = 10^{6.4}$, that there is 0.8 %.

If one considers the equilibria

cis-Cr en$_2$(OH)(H$_2$O)$^{2+}$ + en $\rightleftharpoons$
Cr en$_2$en*(OH)$^{2+}$ + H$_2$O and

cis-Cr en$_2$(OH)(H$_2$O)$^{2+}$ + enH$^+$ $\rightleftharpoons$
Cr en$_2$(enH)(OH)$^{3+}$ + H$_2$O

with the stability constants K_α and K_β, respectively, then the stability ratio between en* and enH$^+$ is $K_\alpha/K_\beta = K_{S2pen}/K_{S2enH_3} = 10^{1.4}$ (Table 3). Assuming this same ratio for en* and enH$^+$ binding to *cis*-Cr en$_2$(H$_2$O)$_2^{3+}$, one finds the stability constant for the reaction

cis-Cr en$_2$(H$_2$O)$_2^{3+}$ + en $\rightleftharpoons$
Cr en$_2$en*(H$_2$O)$^{3+}$ + H$_2$O
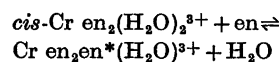
$K_5'' = K_{5cis}'K_\alpha/K_\beta = 10^{1.4}$ M^{-1}, that is nearly the same magnitude as we find for chromium-

(III) and ammonia [10] ($K_5 = 10^{1.6}$ M^{-1}). Also, for silver(I) [21] and mercury(II) [22] it has been found that the stability of the complexes with ammonia and with monodentate ethylenediamine is of the same magnitude.

As mentioned above the method has been applied to other chromium(III) systems and we have, in this way, established equilibrium with, among others, ammonia, EDTA and 1,2-propanediamine.[10] However, the method seems to fail with glycine and non-amine ligands such as oxalate and thiocyanate, where we have so far been unable to build up a steady state with constant chromium(II) concentration, and equilibrium has not been obtained in these cases.

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